Intrasurface Electron Transition Contribution to Energy of Adsorption of Silicon at the SiC(0001) Surface – A Density Functional Theory (DFT) Study

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Abstract
Adsorption of silicon and carbon atoms at polar SiC(0001) and SiC(0001) surfaces at low coverage was studied using ab initio calculations. The single Si atom is adsorbed in the H3 site at both surfaces, saturating broken bonds of the three neighboring atoms. The adsorption of carbon atom at carbon terminated SiC(0001) surface leads to sp² graphene-like reconstruction and the release of silicon atom. The adsorption energy of all constituents is high exceeding 6 eV. The energy barriers for diffusion of all atoms were calculated showing that Si atom is highly mobile at SiC(0001) surface. C adatom at SiC(0001) and Si adatom at SiC(0001) mobility is several order of magnitude lower. C adatom destroys SiC(0001) lattice, thus excess of carbon is detrimental to SiC growth.

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1. Introduction
Silicon carbide properties including high breakdown voltage (~10⁶ V/cm), charge mobility, temperature stability and thermal conductivity, chemical resistance and easy p- and n-type doping select SiC for applications in future electronic technologies [1,2]. Nanopipes, i.e. empty core linear defects are still present in most SiC crystals that hampers SiC based electronic technologies [3-5]. Therefore mechanisms of nanopipes creation in silicon carbide is an important
issue in growth of bulk SiC [9-11]. The nanopipes may be related to the molecular mechanism controlling adsorption of the species during growth from the vapor. Hence adsorption of silicon and carbon at SiC principal faces, denoted as SiC(0001) and SiC(0001), is of high technological importance. The bare, direct cut surfaces are extremely difficult to achieve due to attachment of active species, such as oxygen, hydrogen, water etc., extremely difficult to remove [6]. Therefore the experimental data on clean SiC(0001) and SiC(0001) are scarce.

On the contrary, clean SiC(0001) surface is a convenient starting point for ab initio simulations [7,8]. It was shown that Si-terminated surface does not undergo any reconstruction, but a strong relaxation by inward motion of the two outermost atoms. The electronic structure shows Si broken bond half-filled state in the bandgap, about 1 eV below CBM [8]. These results were confirmed by later simulations by Soltys et al. who found strong relaxation of the topmost layers in the surface for all three basic hexagonal structures [9]. It was also demonstrated that the Si-broken bond related state is located in the bandgap for major SiC structures.

Investigations of SiC(0001) under various coverage identified several surface reconstructions related to nonstoichiometry [10-20]. For excess of silicon these were: $\sqrt{3} \times \sqrt{3}R30^\circ$, 3\times3 [10] 2$\sqrt{3} \times \sqrt{3}$R30$^\circ$, [11] 4\times4 and disordered 1\times1 structure [12], while due to surplus of carbon were: 6$\sqrt{3}$\times$6\sqrt{3}$ [10], 3\times3 [13], c(2 x 2) [14], 6\times6 [15,16], and finally 1\times1 graphite [10, 11, 14, 16]. The latter structure was identified first by Bommel et al. which is considered now as the first evidence of emergence of graphene layer on the SiC(0001) surface [17].

The of $2\sqrt{3} \times \sqrt{3}R30^\circ$ reconstruction was explained using two basic models: the ordered array of Si adatoms, proposed by Kaplan [14] and by Owmann and Martensson [18], and the ordered array of Si surface vacancies, proposed by Bermudez [13] and by Li et al. [19]. The Si adsorption site. was identified as T4 [20,21]. Angle resolved photoelectron spectroscopy (ARPES) provided an evidence of filled surface states located 1.0 eV above valence band maximum (VBM), of the dispersion about 0.2 eV [22]. Further increase of Si coverage leads to the structure typical for Si surfaces [12]. The structures of C-rich surface were governed by transition to six-fold symmetry graphite or graphene structures [12]. Annealing of the $\sqrt{3} \times \sqrt{3}R30^\circ$ SiC(0001) surface at 1300°C leads to emergence of $6\sqrt{3} \times 6\sqrt{3}$ graphene, the process is now used for synthesis of graphene by Si evaporation from the polar SiC surfaces [23].
Northrup and Neugebauer used local density approximation (LDA) \textit{ab initio} calculations proving that $\sqrt{3} \times \sqrt{3}R30^\circ$ structure is related to Si-adatom located in T4 site, the thermodynamically stable configuration in the whole allowed range of silicon chemical potential. Later \textit{ab initio} LDA calculations by Sabisch et al. confirmed Si adatom in T4 site and identified Si broken bond, half-filled in the bandgap [8]. The transition from $\sqrt{3} \times \sqrt{3}R30^\circ$ to $3 \times 3$ structures was linked to drastic decrease of Si adsorption energy from 4.5 eV to 1.6 eV which corresponds to shift from attachment of adatom to the position on top of Si [12]. Starke et al. proposed 3 Si-layer model consisting of Si adlayer, Si-trimer and Si adatom for $3 \times 3$ reconstruction arguing that the twist of Si atoms facilitate reduction of dangling bonds [25].

In this work we summarize the results of intensive \textit{ab initio} calculation regarding the adsorption and energy landscape of Si and C atoms at clean SiC(0001) and SiC(0001) surfaces. Subsequently we investigate Si adsorption at Si-covered SiC(0001) surface accounting the Fermi energy influence [26,27]. This will be summarized by high temperature diagram of Si equilibrium pressure at SiC(0001) surface.

2. Calculation method.

Commercial Vienna \textit{ab initio} simulation package (VASP) was used for \textit{ab initio} simulations of the properties related to presence of silicon and carbon adatoms at the polar SiC(0001) surfaces [27-30]. For the exchange-correlation functional, the generalized gradient approximations (GGA) was applied [31]. The plane wave basis cut-off was set to 500 eV kinetic energy. The Monkhorst-Pack k-point mesh was $8 \times 8 \times 1$ [32]. The 4H-SiC(0001) superlattice slab 8 Si-C bilayers has the two top SiC layers relaxed employing the conjugate gradient algorithm but the cell shape and size was not relaxed. The vacuum space between slab replicas was set to 19.68 Å that assured their quantum isolation. The energy error for the termination of electronic self-consistent (SCF) loop was set equal to $10^{-5}$. These parameters recover basic structural and energetic properties of 4H SiC with good accuracy [9]. The lattice parameters of 4H SiC obtained from the DFT calculations were: $a = 3.094$ Å and $c = 10.129$ Å, compare satisfactorily to the experimental data: $a = 3.073$ Å and $c = 10.053$ Å [2,33,34].

3. Results
The results presented below include adsorption of silicon and carbon at clean SiC(0001) and SiC(0001) surfaces. Subsequently adsorption of silicon at Si-covered SiC(0001) surface is investigated.

3.1. Silicon and carbon at clean SiC(0001) and SiC(0001) surfaces.

Energy of silicon and carbon atoms in function of the distance from clean Si-terminated SiC(0001) surface is presented in Fig. 1. As it is shown, both silicon and carbon atoms are strongly attracted by SiC(0001) surface.

![Energy of silicon (blue squares) and carbon (red diamonds) in function of the distance from Si-terminated SiC(0001) surface. The zero distance is set for the plane of topmost silicon atoms.](image)

The adsorption energies of Si adatom were 6.56 eV and 6.43 eV for H3 and T4 positions respectively. The present results are not compatible with the results reported in Ref. 20,21 where T4 site was suggested as the most stable site. Nevertheless the small energy difference between these two sites indicates as compared to high value of overall adsorption energy indicates that they are close to equivalent.

Further detailed investigations of the energy surface provided more data [35]. It was shown that on-top site corresponds to energy maximum while both H3 and T4 are energy minima. Thus the diffusion of silicon adatoms proceeds by the jumps between these two sites. The energy barriers of 0.40 eV and 0.27 eV were for the jumps from H3 and T4 positions. Thus the silicon
adatoms are highly mobile in the conditions corresponding to Lely growth with the energy close to 2000 K.

The energetic picture of the carbon adatom, approaching SiC surface, shows much stronger attraction, as indicated by the adsorption energy equal to 9.11 eV for H3 site due to much stronger bonding between carbon adatom and the three surface Si atoms. Again the difference between H3 and T4 sites is small as the T4 adsorption energy is 9.01 eV. Thus the sites are again close to equivalent. Due to much stronger bonding, the diffusion barriers are considerably higher. From the transition state energy, these barriers were determined to be equal to 1.13 and 1.03 eV, respectively. Therefore the mobility of carbon adatoms is several orders of magnitude smaller than mobility of silicon at SiC(0001) surface at SiC growth temperatures.

Energy of silicon and carbon atoms in function of the distance from clean C-terminated SiC(0001) surface is presented in Fig. 2. Again, both silicon and carbon atoms are strongly attracted by SiC(0001) surface.

![Graph](image_url)

Fig. 2. Energy of silicon (blue squares) and carbon (red diamonds) in function of the distance from C-terminated SiC(0001) surface. The zero distance is set for the plane of topmost carbon atoms.

Adsorption of silicon atom at C-terminated SiC(0001) surface resembles closely the process on the opposite face. The silicon adatom is located in H3 site with its adsorption energy equal to 7.91 eV. The energy curve is monotonous showing attraction of silicon at relatively large
distance. That confirms creation of strong bonding between Si adatom and the topmost C atoms. The energy landscape shows second minimum at T4 site 0.45 eV above H3 site. The energy barrier deduced from the transition state energy is 0.96 eV and 0.41 eV for jump from H3 and T4 sites.

Drastically different molecular picture is observed for adsorption of carbon atom at SiC(0001) surface. As it was shown the surface undergoes complete structural rearrangement, as indicated by the huge energy jump of about 2.9 eV eV at the distance of 2.75Å. As it was discovered, the surface is reconstructed to $sp^2$ configuration with the detachment of Si atom from beneath the surface atoms [36]. Thus, the question of the preferred adsorption sites and the diffusion of carbon adatom is inappropriate. The surplus of carbon atoms may contribute to creation of other type structures like graphene, as it does not lead to growth of CIC crystals.

The data related to adsorption of Si and C adatoms relevant to growth of SiC crystals by PVT method are collected in Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Surface-site</th>
<th>Adsorption energy [eV]</th>
<th>Barrier to leave the site [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>SiC(0001) - H3</td>
<td>6.56</td>
<td>0.40</td>
</tr>
<tr>
<td>Si</td>
<td>SiC(0001) - T4</td>
<td>6.41</td>
<td>0.27</td>
</tr>
<tr>
<td>C</td>
<td>SiC(0001) - H3</td>
<td>9.11</td>
<td>1.13</td>
</tr>
<tr>
<td>C</td>
<td>SiC(0001) - T4</td>
<td>9.01</td>
<td>1.03</td>
</tr>
<tr>
<td>Si</td>
<td>SiC(0001) - H3</td>
<td>7.91</td>
<td>0.96</td>
</tr>
<tr>
<td>Si</td>
<td>SiC(0001) - T4</td>
<td>7.46</td>
<td>0.45</td>
</tr>
<tr>
<td>C</td>
<td>SiC(0001) - $sp^2$</td>
<td>7.51</td>
<td>NA</td>
</tr>
</tbody>
</table>

The latter line indicates complete reconstruction of C-terminated SiC(0001) under surplus of carbon.

### 3.1. Silicon at Si-covered SiC(0001) surface.

An increase of silicon coverage of SiC(0001) surface leads to two basic effects; crystallographic due to saturation of Si broken bonds by adatoms and the change of Fermi level induced
by the transition of electron between surface states. Since each Si adatom saturates three broken bonds, at the coverage $\theta_{Si} = 1/3$ monolayers (ML), there is no broken bond which reduces the energy gain. The second factor is related to energy contribution arising from the transfer of electrons between surface states after adsorption (intrasurface electron transfer) [26,27]. The dependence of the Si adsorption energy on Si coverage of SiC(0001) surface is presented in Fig. 3.

Fig. 3. Adsorption energy of Si adatoms located in H3 sites at the SiC(0001) surface. The coverage is defined as the ratio of the Si adatoms before adsorption to the number of the Si topmost atoms in the SiC lattice (4 x 4 slab).

From the data analysis it follows that 0.4 eV energy gain at 0 coverage is related to surface reconstruction. Subsequent two points correspond to energy gain of about 6.4 eV, essentially independent on the coverage. The reduction by 1.5 eV is related to electron energy contribution, not present anymore. Further reduction is related to reduction of number of saturated bonds.

4. Conclusions

Ab initio simulations of the clean SiC(0001) and SiC(0001) surface indicate that the most stable position of single Si atom adsorbed at both surfaces is H3 site similar to C adatom at SiC(0001) surface. The energy gain at adsorption of these species is high, exceeding 6 eV/atom. The adsorption of carbon at C-terminated SiC(0001) surface leads to sp$^2$ reconstruction, highly
detrimental to SiC PVT growth. Energy barriers for jumps of adatoms at these surfaces were determined: it is low for Si at SiC(0001) surface - about 0.4 eV, and high for Si at SiC(0001) and C at SiC(0001) - about 1 eV.

Adsorption energy of silicon at Si-covered surface is reduced at 0.25 ML by 1.5 eV due to intrasurface electron transfer and by additional 0.6 eV due to absence of broken bonds at 0.3 ML.

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References